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INFLUENCE OF SOME METALLIC IONS UPON VITAMINS IN FOODS

I. DECOMPOSING EFFECT ON CAROTENE IN THE CARROT

By

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The senior author has reported elsewhere that a remarkably large quantity of metal is dissolved into cooking water from a metallic vessel during cooking (1). It naturally comes into question how it affects the vitamins in foods. The authors have, therefore, undertaken some experiments to investigate it. In this brief paper they intend to report a part of the results concerning the decomposing effect of some metallic ions on carotene in the carrot.

The experiments have been executed under the cordial guidance of Prof. H. Ariyama, for which the authors express their sincere thanks. They have also been indebted to Prof. Mizushima for his kind advice in planning the experiments as well as in statistical analysis of the data.

Methods

As the source of metallic ions the following salts were used:

ferric ammonium sulphate (Fe^{3+}), potassium alum (Al^{3+}), copper sulphate (Cu^{2+}), lead nitrate (Pb^{2+}), zinc chloride (Zn^{2+}), cobalt chloride (Co^{2+}), and manganese sulphate (Mn^{2+}).

Each solution of salt was prepared so as to be at nearly equal metallic ion concentration to that of the corresponding cooking water containing dissolved metal from a vessel in a definite cooking time, (20 minutes), which was confirmed to be ca. 1 mg/100ml in some preliminary experiments. In a case where the relation between the dose of metal and the degree of carotene decomposition was at issue, solutions with higher metallic ion concentrations of 2mg, 5mg and 10 mg/100ml were used. Boiling time of a sample in a solution was not extended over 20 minutes, which was usually long enough for cooking carrots.

A carrot obtained in the market is quartered lengthwise into nearly equal parts, one of which is cut into fine pieces as quickly as possible. After mixing thoroughly, each 2 g of this is taken as a sample, which immediately undergoes treatment.

A randomized block design was adopted. Each experiment consisted of, at least, two and, in most cases, four blocks. A block comprised four plots or treatments including follow procedures keeping in the water (control), boiling in the water, soaking and boiling in a solution, each for 20 minutes. Besides, some additional experiments were made concerning the effect of sodium chloride, Fe^{3+} dose, boiling time and quality of cooking water, the details of which would be given later together with the results.

For the determination of carotene, Fujita's of estimation method of provitamin A was applied (2).

Results

The results obtained are shown in Table 1–5. The statistical analysis has been made exclusively on the E-values determined by Pulfrich's photometer and the actual quantity of carotene is given only when the effect of treatment is significant.

Discussion and Conclusion

In Table 1, the insignificant differences in the mean carotene content between the control and each of the treatments (see Table 1 B) show clearly that simple boiling in the water, soaking and boiling in the solution of copper sulphate, zinc chloride or cobalt chloride do not affect carotene in the sample. In other words, we can say that, so far as the present experimental method is concerned, neither the cations, Cu^{2+}, Zn^{2+} and Co^{2+}, nor the counter anions, SO_4^{2-} and Cl^-, are effective in decomposing carotene each independently or cooperatively. Ferric ammonium sulphate, potassium alum and lead nitrate also seem to exert no noticeable effect when the sample is merely soaked in the solution. When boiled, however, they become effective bringing about a remarkable decrease in the carotene content of the sample as the highly significant difference, I–IV and III–IV, indicate. The situation with manganese sulphate is somewhat different. The carotene in the sample is obviously affected already by simple soaking in its solution (I–III) and its effect is increased by boiling (III–IV), Since SO_4^{2-} is confirmed to be without effect, the decomposing action here is obviously due to the counter cation, Mn^{2+}. With ferric ammonium sulphate, potassium alum and lead nitrate the effect cannot readily be attributable to the metallic ions, Fe^{3+}, Al^{3+} and Pb^{2+}, because the action of the counter ions,

NH_4^+, K^+ and NO_3^-, are unknown. However, additional experiments made with potassium nitrate and ammonium sulphate have revealed that the former significantly affects carotene when the sample is boiled in the solution, while the latter shows no influence upon it. NH_4^+ ion is, therefore, without effect

Table 1. A. Effect of the treatment with various salt solutions at 1 mg/100 ml metallic ion concentration on caroten.

Salts	Blocks	Kept in the water for 20 min. (control) (I)	Boiled in the water for 20 min. (II)	Soaked in the solution for 20 min. (III)	Boiled in the solution for 20 min. (IV)
Ferric ammonium sulphate	I	0.311 0.315 0.299	0.303 0.273 0.300	0.301 0.283 0.283	0.077 0.093 0.145
	II	0.299 0.297 0.322	0.301 0.288 0.291	0.263 0.287 0.311	0.064 0.146 0.134
Average		0.307	0.292	0.288	0.110
Potassium alum	I	0.310		0.289	0.265
	II	0.300		0.284	0.251
	III	0.291		0.293	0.270
	IV	0.293		0.300	0.284
Average		0.299		0.291	0.268
Copper sulphate	I	0,603	0.521	0.539	0.522
	II	0.541	0.518	0.515	0.500
	III	0.489	0.468	0.472	0.461
	IV	0.523	0.504	0.491	0.497
Average		0.531	0.503	0.504	0.495
Lead nitrate	I	0.321	0.312	0.310	0.294
	II	0.316	0.314	0.314	0.288
	III	0.339	0.331	0.308	0.304
	IV	0.432	0.424	0.412	0.403
Average		0.352	0.345	0.336	0.322
Zinc chloride	I	0.342		0.338	0.339
	II	0.301		0.303	0.299
	III	0.351		0.350	0.342
	IV	0.350		0.350	0.346
Average		0.336		0.335	0.332
Cobalt chloride	I	0.392		0.389	0.390
	II	0.393		0.385	0.375
	III	0.438		0.432	0.428
	IV	0.446		0.422	0.420
Average		0.417		0.407	0.403
Manganese sulphate	I	0.291		0.234	0.172
	II	0.291		0.242	0.172
	III	0.299		0.237	0.175
	IV	0.296		0.231	0.183
Average		0.294		0.236	0.175

B. Test of significance of difference in the mean carotene content between the treatments.

Salts	Differences of the mean			
	I–II	I–III	I–IV	III–IV
Ferric ammonium sulphate	0.014	0.019	0.197***	0.178***
Potassium alum	—	0.008	0.031**	0.023*
Copper sulphate	0.028	0.027	0.036	0.009
Lead nitrate	0.007	0.016	0.030***	0.014**
Zinc Chloride	—	0.001	0.004	0.003
Cobalt chloride	—	0.010	0.014	0.004
Manganese sulphate	—	0.033***	0.119***	0.086***

Note : *, ** and *** denote the significance levels showing less than 5%, 1% and 0.1 % respectively. The same applies to Tables 2–5.

C. Actual quantity of carotene represented by γ in 100 g of fresh carrot.

Salts	Control I	I–III	I–IV	III–IV
Ferric ammonium sulphate	7921±232	—	5083±335	4592±335
Lead nitrate	9082± 65	—	774±103	361±103
Manganese sulphate	7585± 52	851± 75	3070± 75	2219± 75
Potassium alum	7714±121	—	7508±180	6914±180

Table 2. A. Effect of boiling time on carotene in the solutions at 2 different Fe^{3+} concentration.

Fe^{3+} concentration	Blocks	Control (I)	Boiled for		
			5min. (II)	10min. (III)	20min. (IV)
2mg/100ml	I	0.407	0.349	0.332	0.203
	II	0.427	0.396	0.330	0.236
Average		0.414	0.373	0.331	0.220
5mg/100ml	I	0.334	0.260	0.138	0.094
	II	0.325	0.250	0.128	0.070
Average		0.330	0.255	0.133	0.082

B. Test of significance of differences between the means.

Fe^{3+} concentratration	I–II	I–III	I–IV	II–III	III–IV
2mg/100ml	0.041	0.083*	0.194**	0.042	0.112**
5mg/100ml	0.075*	0.197**	0.248***	0.122**	0.051*

C. Actual quantity of carotene (γ in 100 g of fresh carrot)

Fe^{3+} concentration	control I	I–II	I–III	I–IV	II–IV	III–IV
2mg/100ml	10681±284	—	2141±387	5005±387	—	2890±387
5mg/100ml	8514±284	1935±403	4983±403	6398±403	3148±403	1316±403

Table 3. A. Effect of Fe^{3+} concentration on carotene during 10 minutes boiling.

Blocks	Control (I)	Fe^{+3} ion concentration		
		2mg/100ml (II)	5mg/100ml (III)	10mg/100ml (IV)
I	0.453	0.351	0.214	0.192
II	0.466	0.377	0.214	0.197
III	0.463	0.391	0.211	0.172
IV	0.464	0.387	0.219	0.209
Average	0.462	0.377	0.215	0.193

B. Test of significance of differences between the means.

I–II	II–III	III–IV
0.085***	0.162***	0.022*

C. Actual quantity of carotene (γ in 100 g of fresh carrot)

Control I	I–II	II–III	III–IV
11920±142	2193±206	4170±206	568±206

Table 4. A. Effect of well water and city water (from the water works) on carotene before and after bioling.

	Control (I)	Boiled in the raw water for 20 min. (pH=7.0) (II)	Boiled in the once-boiled water for 20 min. (pH=7.5) (III)
Well water	0.385 0.391 0.332	0.331 0.342 0.278	0.315 0.310 0.236
Average	0.369	0.317	0.287
City water	0.396 0.388 0.405 0.413	0.355 0.354 0.315 0.313	0.370 0.373 0.339 0.335
Average	0.401	0.334	0.354

B. Test of significance of differences between the means.

	I-II	I-III	II-III
Well water	0.052**	0.082***	0.030**
City water	0.067**	0.047*	0.020

C. Actual quantity of carotene (γ in 100 g of fresh carrot)

	Control I	I-II	I-III	II-III
Well water	9620±129	1342±168	2116±168	774±168
City water	10246±232	1729±335	1213±335	—

Table 5 A. Effect of NaCl at two different concentration on carotene by boiling for 20 min.

Blocks	Control (I)	Concentration of NaCl 1 % (II)	Concentration of NaCl 2 % (III)
I	0.325	0.277	0.266
II	0 317	0.267	0.270
III	0.315	0.256	0.270
IV	0.323	0.257	0.256
Average	0.320	0.264	0.265

B. Test of significance of differences between the means.

I	I-II	I-III
0.056***	0.055***	0.001

C. Actual quantity of carotene (γ in 100 g fresh carrot)

Control I	I-II	I-III
8250±175	1445±245	1419±245

and the action of ferric amonium sulphate is ascribable to Fe^{3+}. On the other hand, the results with sodium chloride given in Table 5 show an obvious effect of Na^+ ion on carotene. So, it might perhaps be said that in the case of potassium nitrate, K^+ is responsible for the decomposition of carotene and so with Pb^{2+} in the case of lead nitrate, NO_3^- being inactive in both cases. However, it still remains unexplained whether Al^{3+} from potassium alum is effective or not, which will be confirmed by the authors in their future studies.

In Table 2 one can see the effect of boiling time on carotene at two different levels of Fe^{3+} concentration, 2 mg and 5 mg/100 ml. From the significant differences given in Table 2 B it can be said that the longer the boiling time the more carotene is decomposed and that the effect of boiling is larger in the case of higher ion concentration than in that of lower concentration. Decomposition of carotene is also accelerated as the concentration of effective ion becomes higher. The situation is well illustrated by the results presented in Table 3, where the effect of three different doses of Fe^{3+} during 10 minutes' boiling is given.

Carotene is affected also by the nature of cooking water used. As shown in Table 4, boiling a sample in well water as well as in city water causes a significant decrease in its carotene content, whether the water is boiled beforehand or not. Although no investigation has been made in this respect, the effect might be due to some metals contained in them, say, iron from the water-main in the case of city water.

In cooking carrot, sodium chloride is frequently used and its influence on carotene cannot be overlooked. Table 5 presents the results at two different sodium chloride concentrations in 20 minutes' boiling, which clearly shows its effectiveness. Since, as already confirmed, Cl^- has no influence on carotene, the effect here is, no doubt, due to Na^+. No significant difference in the degree of carotene decomposition is, however, noted between the two levels of concentration, 1% and 2%.

Summing up the above-described, we can conclude the following : In soaking or boiling a carrot for a time not extending over 20 minutes in a solution containing a metallic ion at the concentration of 1 mg/100ml, 1) Cu^{2+}, Zn^{2+} and Co^{2+} have no influence upon carotene in the carrot ; 2) Fe^{3+} and Pb^{2+} are effective in decomposing carotene only when the carrot is boiled ; 3) Mn^{2+} affects carotene by simple soaking and its effect is increased by boiling ; 4) Na^+ and, perhaps, K^+ are also effective when boiled ; 5) With Fe^{3+} in the concentration range between 1 mg and 10 mg/100ml under 10 minutes' boiling, the carotene decomposing effect increases as the concentration becomes higher ; 6) In the boiling time range between 5 and 20 minutes the effect becomes larger as the time becomes longer ; 7) The counter anions, SO_4^{2-} and Cl^-, are without effect in decomposing carotene and perhaps the same is true with NO_3^-. The counter cation, NH_4^+, is also confirmed to have no effect ; 8) The action of Al^{3+} is not clear.

Summary

Influence of metallic ions upon carotene in the carrot was investigated using various solution of salts at the metallic ion concentration of 1 mg/100ml. Cu^{2+}, Zn^{2+} and Co^{2+} proved to have no effect on carotene even if the sample of finely chopped carrot was boiled in the solution during 20 minutes. Fe^{3+} and Pb^{2+} were effective in decomposing carotene when the sample was boiled in the

solution. Mn^{2+} affected carotene when the sample was merely soaked in the solution and its effect was increased by boiling. When the concentration of Fe^{3+} was constant, the carotene decomposing effect of a solution became greater as the boiling time became longer. When the boiling time was constant the effect became greater as the concentration of ion became higher. Na^+ and, perhaps, K^+ ions were also effective under boiling. The counter ions such as SO_4^{2-}, Cl^- and NH_4^+ were confirmed to be without effect and, perhaps, the same is ture of NO_3^-.

References

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2) Fujita, S. (1948). "Chemical Method of Vitamins" P. 63, Seibundoshinkosha, Tokyo.